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Allan, Francis Barclay

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By F. B. Allan.

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THE BASIC NITRATES OF BISMUTH.

Thesis

Presented to the Senate of the University of Toronto for the degree of Doctor of Philosophy.

BY

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F. B. ALLAN.

Reprinted from the American Chemical Journal, April, 1901.

To the REGISTRAR.

Dear Sir,

I have carefully examined the thesis sent me by Mr. F. B. Allan, B.A., for the degree of Ph.D., and have pleasure in recommending that it be accepted as qualifying for that degree.

Yours faithfully,

(Sgd) W. R. LANG,
Prof. Chem.

May 6, 1901.

I hereby certify that the thesis above mentioned has been accepted by the Senate of the University of Toronto for the degree of Doctor of Philosophy in accordance with the terms of the statute in that behalf.

JAMES BREBNER,
Registrar.

The University of Toronto,
June 5, 1901.

[Reprinted from the American Chemical Journal, Vol. XXV. No. 4. March, 1901.]

THE BASIC NITRATES OF BISMUTH.

By F. B. Allan.

When bismuth nitrate is treated with water, it is decomposed, forming a basic nitrate, $BiONO_3$, which has been described by Duflos,[1] Heintz,[2] Becker,[3] Ditte,[4] and others. It is said to have one, two, or three molecules of water of crystallization, according to the method of preparation.

Numerous other basic nitrates have also been described :

A. $6Bi_2O_3.5N_2O_5 + 9H_2O$.—Bismuth nitrate, or a solution of bismuth in nitric acid, is added to water above 50° (Becker).

B. $5Bi_2O_3.4N_2O_5 + 9H_2O$.—A solution of bismuth nitrate is added to water at 40° to 50° ; after twenty-four hours three-quarters of the liquid is poured off and more water at 50° is added ; when the liquid has cleared, the precipitate is filtered off and washed with cold water (Becker).

C. $11Bi_2O_3.9N_2O_5 + 21H_2O$.—Same preparation as *B* (Janssen).[5]

D. $4Bi_2O_3.3N_2O_5 + 9H_2O$.—*A* is washed till the wash-water gives no acid reaction (Becker).

E. $5Bi_2O_3.3N_2O_5 + 8H_2O$.—(*a*) The salt $BiONO_3$ is dissolved in a large quantity of water which, after some time, deposits a precipitate without crystalline structure (Becker).

(*b*) The salt $BiONO_3$ is mixed with twenty-four times its weight of water and dilute sodium hydroxide is added till the liquid scarcely reddens litmus (Duflos, Janssen).

F. $2Bi_2O_3.N_2O_5 + H_2O$.—The salt $BiONO_3$ is decomposed by water at 100° (Ditte).

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[1] Archiv. der Pharm., [2], **23**, 307 ; Pharm. Centrbl., 1840.

[2] J. prakt. Chem , **45**, 102.

[3] Archiv. der Pharm., **55**, 31, 129 ; Ann. Chem. (Liebig), **68**, 282.

[4] Compt. rend., **79**, 956.

[5] Archiv. der Pharm., **68**, 1, 129 ; Forts. der Chem., 1851.

It will be seen that, in most of the above preparations, no account of the composition of the mother-liquor is given. Ditte has shown that water at 10° will decompose the neutral nitrate, giving the so-called subnitrate ($BiONO_3$), only until it contains 83 grams of nitric anhydride per liter, and that a nitric acid solution stronger than that does not decompose bismuth nitrate. He also found that, at 100°, the change from the form $BiONO_3$ to the form $2Bi_2O_3.N_2O_5$ took place only when the water contained less than 4.5 of grams of nitric anhydride per liter, and that this reaction was reversible, the subnitrate being again formed when more acid was added to the solution.

The directions for preparing some of these basic nitrates were followed, and Table *A* contains a comparison of the products with those analyzed by Becker and Janssen. The bismuth was estimated as oxide by ignition of the basic nitrate, or, if in solution, by boiling with an excess of a solution of sodium carbonate and ignition of the precipitate, or by evaporation of the solution to dryness and ignition of the residue. The nitric acid was determined by boiling for half an hour with an excess of a solution of sodium carbonate, and estimation of the excess after filtering.

Table A.

			Becker.		Janssen.	
	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.	Bi_2O_3.	N_2O_5.
A	79.65	16.81	79.86	15.55		
B,*C*	78.95	15.93	79.6	14.6	80.17	14.0
D	80.16	15.11	79.2	13.8		
E(*b*)	83.14	12.71	84.3	11.8		

This indicates that the composition of the different products is dependent on conditions which have not been described, and that possibly an examination of these conditions would show that some of these basic nitrates are mixtures. Janssen has endeavored to represent them all as consisting of

$$Bi(NO_3)_3 + 5H_2O \text{ and } 5Bi_2O_3.3N_2O_5 + 8H_2O$$

in varying proportions.

Prof. Miller suggested to me the application of the "phase rule" to this problem. In a system containing bismuth oxide, nitric anhydride, and water, five phases would constitute a nonvariant system, and a liquid, a gas, and three solid phases could exist only at one temperature, one pressure, and one concentration of the liquid for any three given solid phases. If the system consisted of a liquid, a gas, and two solid phases, it would be monovariant, and we might have such a system at different temperatures or with different concentrations of the liquid, but, at any given temperature, the liquid in equilibrium with two given solid phases could not vary in concentration. In a divariant system, one solid phase might be in equilibrium, at constant temperature, with a liquid of varying concentration, or with a liquid of given concentration at different temperatures. A knowledge of the conditions of equilibrium in such a system will enable us to determine whether one or two solid phases are present.

Neutral bismuth nitrate, or a basic nitrate of known composition, was added to water or a solution of nitric acid, and stirred in a water-bath, at constant temperature, till equilibrium was reached. It was found that these reacted more quickly than bismuth oxide and nitric acid. The stirrer was driven by a water motor and had bottles on both sides of a horizontal shaft in such a way that the contents were thrown from one end of the bottle to the other. The acidity of the liquid was determined from time to time, and when this had become constant the bismuth oxide in solution was also determined, and the difference between the bismuth oxide and nitric anhydride used, and the amount of these in solution gave the composition of the solid contents of the bottles.

The bismuth nitrate used was Kahlbaum's preparation, and the basic nitrate used in the first series of experiments was prepared from it by adding the solution in nitric acid to a large volume of cold water and filtering off the precipitate as soon as it had settled to the bottom of the vessel. There seems to be no difficulty about the preparation of this substance, as repeated experiments gave the same product. One specimen which had been dried in the air for a week gave the following results on analysis :

	Calculated for $BiONO_3 + H_2O$.	Found.
Bi	68.37	68.25
NO_3	20.35	20.30

Table B.

Temp., 21°. $\frac{Bi_2O_3}{N_2O_5}$ in $BiONO_3 = 4.31$; in $6Bi_2O_3.5N_2O_5 = 5.17$.

No.	Salt used.	Components used.			Acidity of liquid.		Bi_2O_3 in solution. Grams.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	6 days. N.	13 days. N.		
1	$BiONO_3$	1.52	0.351	40	0.0293	0.0293	....	5.24
2	"	3.04	0.703	40	0.054	0.054	....	5.15
3	"	4.56	1.054	40	0.085	0.085	....	5.22
4	"	7.59	1.757	40	0.144	0.145	....	5.25
5	"	1.52	0.673	40		0.184	0.08	5.16
6	"	3.04	1.025	40		0.212	0.10	5.15
7	"	4.55	1.376	40		0.244	0.14	5.17
8	"	6.07	1.727	40	0.267	0.277	0.16	5.21
9	"	1.52	0.866	40		0.283	0.17	5.13
10	"	3.04	1.217	40		0.318	0.21	5.25
11	"	4.56	1.568	40	0.312	0.349	0.28	5.09
12	"	6.07	1.92	40	0.328	0.377	0.31	5.00
13	"	7.59	2.27	40	0.347	0.385	0.37	4.91
14	$Bi(NO_3)_3$	1.74	1.21	40.7		0.426	0.45	4.44
15	"	2.35	1.65	40.9		0.582	0.75	4.32
16	"	2.87	2.01	41.1	0.716	0.717	1.04	4.35

It will be seen that the contents of most of the bottles had come to equilibrium, but Nos. 11, 12, and 13 were still changing. Nos. 1 to 10 had solid contents of constant composition in equilibrium with liquids of different concentrations, and these, therefore, contained but one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 14 to 16 also contained one solid phase, $BiONO_3$. Nos. 11 to 13 contained the salt $BiONO_3$ partially converted into the salt $6Bi_2O_3.5N_2O_5$, but, as equilibrium had not been reached, the liquid phase was not of constant concentration.

A quantity of the salt $6Bi_2O_3.5N_2O_5$ was prepared by stirring the salt $BiONO_3$ with water, care being taken that the mother-liquor was of a concentration found by the previous experiment to be in equilibrium with that compound. This was used in some of the bottles in the next series. A higher temperature was now used in order that more basic nitrates might be obtained, and, also, that equilibrium might be more quickly reached.

Table C.

Temp. 50°. $\frac{Bi_2O_3}{N_2O_5}$ in $2Bi_2O_3.N_2O_5 = 8.63$.

No.	Salt used.	Components used.			Acidity of liquid.			Bi_2O_3 in solution.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	6 days. N.	13 days. N.	19 days. N.	Grams.	
1	$6Bi_2O_3.5N_2O_5$	1.53	0.295	40.2	0.057	0.056	0.057	....	8.74
2	"	2.30	0.443	40.3	0.080	0.080	0.081	....	8.59
3	"	3.06	0.590	40.4	....	0.109	0.108	....	8.50
4	"	3.83	0.730	40.5	1.36	....	0.135	0.03	8.63
5	"	4.60	0.873	40.6	1.60	0.159	0.159	0.04	8.64
6	"	6.12	1.164	40.9	....	0.217	0.216	0.07	8.76
7	"	7.66	1.451	41.1	....	0.265	0.265	0.11	8.67
8	"	9.20	1.75	41.3	0.275	0.284	0.286	0.13	8.09
9	"	11.49	2.18	41.6	0.270	0.284	0.283	0.13	7.33
10	"	15.32	2.90	42.2	0.235	0.270	0.276	....	....
11	$BiONO_3$	3.79	0.88	40	0.075	0.242	0.251	....	....
12	"	7.59	1.75	40	0.144	0.193	0.286	0.13	6.27
13	"	11.38	2.63	40	0.216	0.217	0.215	0.08	(5.20)
14	"	15.18	3.51	40	....	0.286	0.284	0.13	5.18
15	"	11.38	2.63	25	....	0.350	0.352	0.17	5.20
16	"	15.18	3.51	25	....	0.467	0.466	0.22	5.17

In this series, Nos. 1 to 7 contained one solid phase, $2Bi_2O_3.N_2O_5$, and Nos. 14 to 16 also contained one solid phase, $6Bi_2O_3.5N_2O_5$. Nos. 8, 9, and 12 were a monovariant system and contained varying proportions of the salts $2Bi_2O_3.N_2O_5$ and $6Bi_2O_3.5N_2O_5$ in equilibrium with liquids of the same composition, as we may neglect the possibility of this being the temperature and concentration at which a nonvariant system can exist. In Nos. 10, 11, and 13, at the first analysis, the solid contents had changed from the form $BiONO_3$ to the form $6Bi_2O_3.N_2O_5$, and the reaction seems to have halted there. They were then seeded with the salt $2Bi_2O_3.N_2O_5$ and, at the end of thirteen days, the reaction had proceeded further in Nos. 11 and 12, but in No. 13 further action had not begun in nineteen days. The same result was observed if the experiment was begun with one of the basic nitrates, and a solution of nitric acid instead of water. No reaction took place for days, the length of time before the reaction began depending on the concentration of the nitric acid.

A series of experiments was begun at 75°, but only three measurements were obtained, as all the other bottles broke at that temperature.

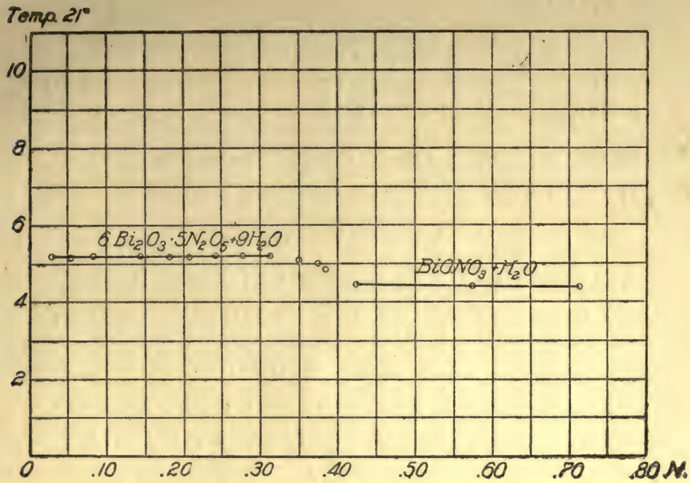
Table D.

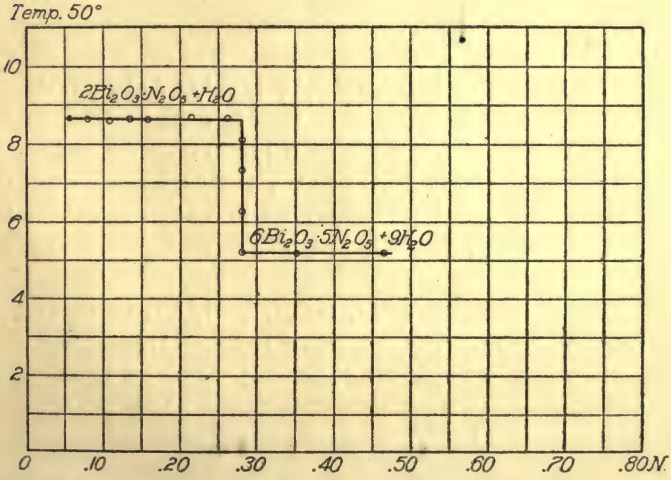
Temperature 75°.

No.	Salt used.	Components used.			Acidity of liquid, 2 days.	Bi_2O_3 in solution.	$\frac{Bi_2O_3}{N_2O_5}$ in solid.
		Bi_2O_3. Grams.	N_2O_5. Grams.	H_2O. cc.	N.	Grams.	
1	$6Bi_2O_3.5N_2O_5$	3.06	0.59	40.4	0.109	0.03	8.65
2	"	6.13	1.16	40.9	0.208	0.05	8.68
3	"	9.19	1.75	41.3	0.314	0.15	8.61

If we represent the results given in Tables *B* and *C* in diagrams taking as abscissae the concentration of nitric acid in the liquids in the different bottles expressed in terms of a normal solution, and as ordinates the relation between bismuth oxide and nitric anhydride in the solid contents, horizontal lines represent divariant systems consisting of one solid, a liquid, and a gas, and perpendicular lines represent monovariant systems consisting of two solids, a liquid and a gas. The concentration of the gaseous phase is a function of the concentration of the liquid. In the diagram representing

Table *B* there is no perpendicular line because equilibrium had not been reached in the bottles whose contents are represented between the two horizontal lines.





The solid contents in Nos. 1 to 7, Table *C*, and also those in Nos., 14 to 16 in the same series, were filtered off and dried between filter-paper. An analysis of these two products gave the following results :

	Calculated for $6Bi_2O_3.5N_2O_5 + 9H_2O =$ $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$.	Found.
Bi	71.65	71.70
NO_3	17.77	17.81

	Calculated for $2Bi_2O_3.N_2O_5 + H_2O =$ $Bi_4O_5(NO_3)_2 + H_2O$.	Found.
Bi	78.97	78.86
NO_3	11.76	11.80

Both were impalpable white powders and neither lost in weight when heated for some hours at 100°.

Conclusions.

1. Pouring nitric acid solutions of bismuth into water at ordinary temperature gives only the salt $BiONO_3 + H_2O$ if the precipitate be quickly filtered off, even when the resulting mother-liquor is such as is in equilibrium only with a more basic nitrate. This is due to the fact that where the strong acid solution meets the water and the salt $BiONO_3 + H_2O$ is formed, the concentration of the acid is high, and when the crystalline precipitate comes in contact with the weaker acid the reaction is too slow to produce an appreciable change in a few hours.

2. At 21°, the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ is in equilibrium with nitric acid solutions from 0.03 to 0.32 normal, and the salt $BiONO_3$ with solutions from 0.425 to 0.72 normal.

3. At 50°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with nitric acid solutions from 0.057 to 0.285 normal, and the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ with solutions from 0.285 to 0.466 normal.

4. At 75°, the salt $Bi_4O_5(NO_3)_2 + H_2O$ is in equilibrium with solutions of nitric acid from 0.109 to 0.314 normal.

5. That no basic nitrate containing a greater proportion of nitric anhydride than the salt $Bi_4O_5(NO_3)_2 + H_2O$ and less than the salt $Bi_{12}O_{13}(NO_3)_{10} + 9H_2O$ exists at 50°, although at least two were said to have been prepared at that temperature.

6. That the slowness of the reaction, or a concentration of the mother-liquor at which a monovariant system was possible, accounts for the many basic nitrates which have been described.

7. That reaction between the higher basic nitrates and water containing nitric acid begins only after some time.

THE CHEMICAL LABORATORY OF
THE UNIVERSITY OF TORONTO,
January, 1901.

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